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SHAPE MEMORY ALLOYS - NEW MATERIALS FOR FUTURE ENGINEERING?

E. Hornbogen

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16. Abstract

A review with 24 references is given on shape-memory alloys including properties, production, applications and fundamental principles of the shape memory effect.

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SHAPE MEMORY ALLOYS--NEW MATERIALS FOR FUTURE ENGINEERING?

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Shape memory is a new material property. An alloy which experiences relative severe plastic deformation resumes its original shape again after heating by 10 - 100 °C. Besides simple shape memory, in similar alloys there is the second effect where the change in shape is caused exclusively by little temperature change. In pseudo-elasticity, the alloy exhibits a rubber-like behavior, i.e. large, reversible deformation at little change in tension. β-Cu and β-NiTi alloys have been used in practice. The probability is that soon alloys based on Fe will become available (Table 1). Recently increasing applications for this alloy were found in various areas of technology, even in medical technology. Japan, the USA and recently also China are leaders in this area. Stronger and coordinated efforts in our country are being recommended.

1. Shape Memory Alloys (SMA) are Materials with New, not merely Improved, Properties.

Today it is generally known that new or improved materials are essential for future developments in engineering. This is expressed most clearly through semiconductor materials and their role in revolutionizing electronics. But there are many other,

*Numbers in margin indicate pagination of foreign text.

less known examples. We mention only one other case--the cutting materials. The development of fast working steels --> hard sinter metals --> CVD composite systems--considerably promoted and changed milling engineering. For our subject it is essential to distinguish two types of material developments:

1. Improvements to known properties
2. Discovery of entirely new properties.

Examples of case 1 are the increase in elastic limit and fracture strength of construction materials, increasing the heat resistance of high temperature materials or reducing he Watt losses of transformer plates. In these cases, as a rule there are no great problems in acceptance of the new materials by the design engineer, i.e. in the interface between material and design.

The alloys with shape memory belong to the second group. They are not quite easy to produce and their properties are new. Consequently, there are greater restrictions along the path from research in materials science to alloy preparation to technical application. Since the first description of the notable properties of β-CuZn [1] and β-NiTi [2, 3] alloys, a long time has elapsed.

In a more difficult evolutionary process, several materials producers have since begun to prepare semifinished goods for their own applications. Prediction of the future is always risky. At present it looks as if there will be no "breakthrough", but a very much more rapid spread of the application of SMA, both on many areas of conventional engineering, for new technologies, but also

Table 1. The Most Important Alloy Groups and Structure of the High Temperature Phase β.

Legierung 1	2 Struktur der Hochtemperaturphase β	
CuZn	krz	geordnet 3
CuZnAl	"	"
CuAlNi	"	"
NiTi	"	"
NiTiCu	"	"
NiTiFe	"	"
FePt	krz	"
FePd	"	"
FeNiAl	"	teilweise geordnet 4
FeNiAlTi	"	"
FeNiCoTi	"	"
FeMnS	"	ungeordnet 5
TiNiCu	krz	"

Key: 1-alloy 2-structure of the high temp. phase 3-ordered 4-partly ordered 5-not ordered

in more distant areas ranging from medical implantations to the clothing industry.

In August and September 1986 three conferences were held and devoted exclusively or primarily to the area of science and applications of SMA [4, 5, 6]. If we consider the conference sites and take into consideration that the most important American manufacturer (Raychem, Menlo Park, California) is centered on the West Coast, then it is clear where today the emphasis of developments in SMA will take place--in the Pacific Basin.

The notable properties of SMA must naturally be known to the design engineer before he can begin to imagine potential applications. The same also applies for their limitations. So an intensive cooperation between material scientists and design engineers is expedient. The special properties will be described below. In supplement to this, a selection of earlier publications will be given which all pertain to properties of these alloys and which will also provide many other details [7-12].

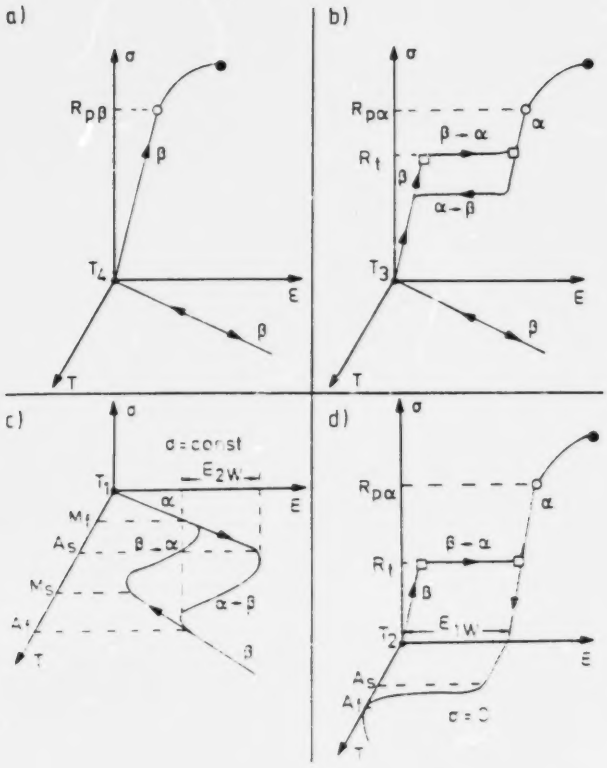

Fig. 1a-d: Stress, Deformation, Temperature Diagrams (σ, ε, T). a) Behavior of a conventional material with permanent deformation above R_p. Break at R_m, constant thermal expansion. b) Pseudo-elasticity: Under stress above R_t a strong shape change occurs, which recedes upon release at a somewhat smaller stress $\sigma = R_t - \Delta\sigma_H$. c) Two-way effect: When heating, a shape change takes place between A_s and A_r which first has to be "trained". Upon cooling, it is again made retrograde between M_s and M_f (σ, ε). d) One-way effect: At R_t an (apparent) permanent deformation occurs ε_t (σ, ε), upon subsequent heating, the shape change between A_s and A_f recedes completely (ε, T).

The shape memory effect (SME) pertains to the shape change of the material with change in its temperature, with or without the effect of external mechanical stresses. In Figures 1a-d the potentials of such behavior are presented.

Figure 1a shows the known behavior of a common construction material (steel, Al-alloy). Under stress, e.g. in a tensile test, reversible, elastic shape change is followed by irreversible, plastic deformation and fracture then occurs. In a temperature change, the length changes reversibly per the thermal expansion coefficient, similar to elastic deformation.

Figures 1b-d show the three special properties of SMA:

b) Pseudoelasticity (PE)

c) One-way effect (1W)

d) Two-way effect (2W)

In the 1W effect the material is apparently plastically deformed at a stress $R_t < R_p$. Upon subsequent heating above a certain temperature A_s, it begins to remember its original shape in the undeformed state (Fig. 2). The temperature range for this effect can be adjusted through chemical composition and lattice of alloys in a broad range from 0 K up to about 500 K (Table 2). For the 2W effect the shape change occurs solely due to change in temperature. The maximum amount of shape change is always somewhat less than for the 1W effect (Table 2). Compared to normal thermal shape change, it is notable that it occurs nearly discontinuous in a small temperature range and with a hysteresis ΔT_h, which also can be adjusted between a few and over one hundred degrees. In accord with the selected boundary conditions, the material can complete a motion ($\sigma = 0$) or exert a force ($\varepsilon = 0$). Finally, there is still pseudoelasticity, where the metal exhibits a rubbery behavior. In a stress $\sigma = R_t$, a strong deformation

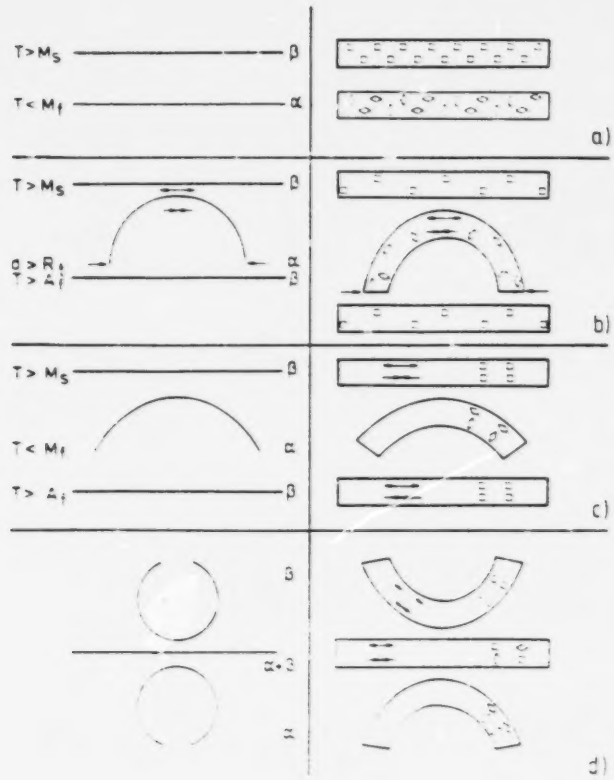

Fig. 2a-d: Shape Change (Bending) of SMA under Different Conditions. a) No shape change upon transition without stress effect. b) One-way effect, β .--> -transition under stress or -deformation of the Martensite (see Fig. 3b). c) Two-way effect. d) "wrapping effect (all-around effect). (Arrows: internal or external stresses; β ; austenite; α', Martensite and its orientation.

occurs as for the 1W effect. But upon relief it recedes semi-elastically. So like rubber, large deformations with little change in tension will occur. This is again connected with stress hysteresis $\Delta\sigma_h$ (Fig. 1b).

Finally it is important that depending on the direction of the external stress, a stretching or compression takes place. Consequently, bending and complicated movements can be performed by a SMA wire (which would require a number of ball joints in conventional components) (Fig. 2, 3, and 4).

Table 2. Some Characteristic Properties of Cu-based and NiTi alloys.

				β-NiTi	β-CuZnAl
1 Dichte	ϱ	$\frac{g}{cm^3}$		6.5	7.5
2 el. Leitfähigkeit	σ	$10^6 \frac{S}{m}$		1	10
3 Zugfestigkeit	R_m	MPa		800	500
4 rel. Formänderung (Einweg)	ε_{rev}	%		6	4
4 rel. Formänderung (Zweiweg)	ε_{rev}	%		4	2
7 max. Gebrauchstemperatur	T_{max}	°C		400	200

Key: 1-density 2-elec. conductance 3-tensile strength 4-rel. shape change 5-one way 6-two way 7-max. use temperature

2. Some Required Materials Fundamentals

The discovery and development of these new alloy groups is based solely on scientific research. This distinguishes them from materials (e.g. bronze, steel, cast iron) which have thousands of years of empirical development behind them. The prerequisite for the occurrence of the SME (Fig. 1 and 2) is a martensite transition from a crystalline structure β into a new α and vice-versa. The conversion occurs through a shear process (Fig. 3) [11, 12]. It occurs without diffusion and can thus occur down to very low temperatures. The transition temperatures are defined not only by thermodynamic equilibrium (determines primarily the chemical composition of the alloy), but also by the mechanical properties of the phases, which in turn can be affected by the lattice.

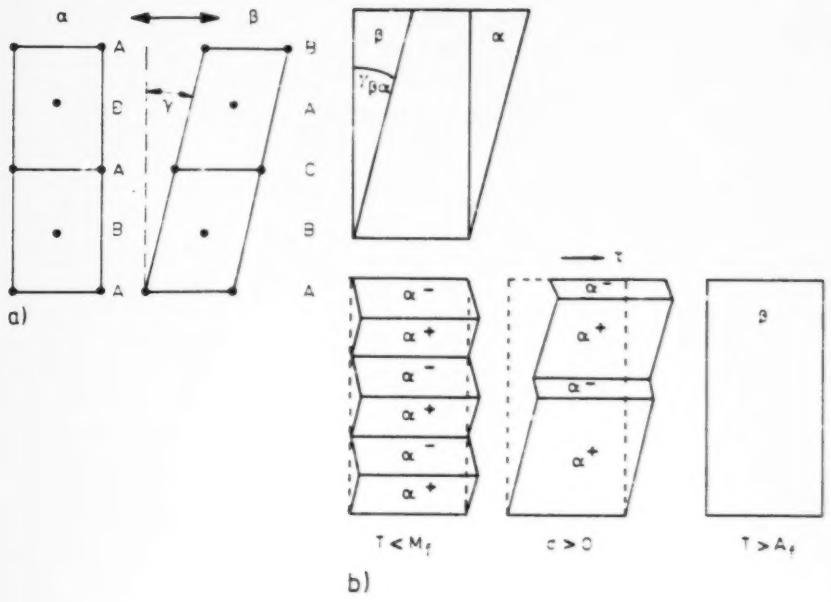

Fig. 3a-b. Crystallographic Aspects of Martensite Transition. a) Transition: cubic surface centered α <--> hexagonal densest packing β (example: FeMnSi, Table 1). The ranking of (111) α -planes, ABCABC changes into ABABAB... From the shear angle $\gamma \equiv \gamma_{\beta\alpha} \approx 2\varepsilon_{max}$ we obtain the upper limit of shape memory ε_{max} (Table 4c). b) Crystallography of shape memory for transition β --> α and for the deformation of α with twin lattice $\alpha^+ \rightarrow \alpha^-$, schematic.

One property of martensite transition is that it can be triggered in a temperature range $M_s < T_m < M_d$ by means of an external shear stress. Figures 4a-b show the typical profile of this transition and the designations used in SMA engineering for the transition temperatures. The 1W effect thus can be attributed to the stress induced β --> α, followed by the retransition α--> β upon heating. One variant is the deformation of martensite by shifting the twin crystal (Fig. 3b). This shape change is also reversible upon subsequent transition α--> β. It is essential that from a number of crystallographic shear systems, a few are selected which are favorable for the external shear

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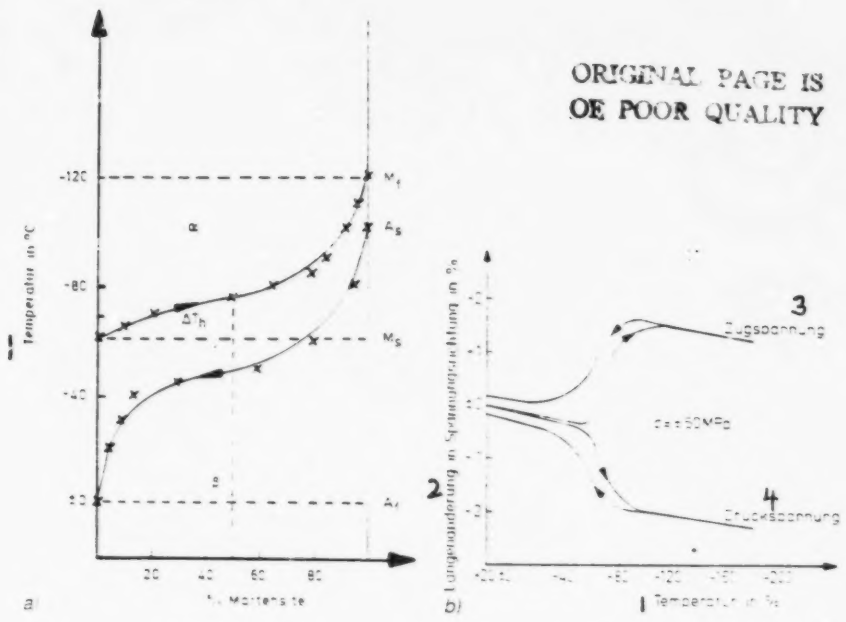

Fig. 4a-b. Examples for the Profile of Reversible Martensite Transitions (Cu +60.80 % by weight Zn), transformed fraction f_α (from [1]). a) Symbols for transition temperature, Table 4a (measured by x-ray). b) Expansion or contraction of material, depending on whether the transition occurs under tensile or compressive stress (ε, T).

Key: 1-temperature 2-length change in stress direction 3-tensile stress 4-compressive stress

stress. This transition shear determines the upper limit of the pseudoelastic or plastic deformation (theoretical shear $\gamma \approx 2\varepsilon_{max}$).

The two-way effect requires no external forces. The martensite transition in this case is affected through internal stresses or preformed heterogeneous germ centers so that a shape change due to oriented trasition occurs. In practice this is done by "training". The material is bent back and forth repeatedly in the direction of the desired shape change. The training effect can be intensified in many alloys by segregation treatment under

tension which fixes the internal stress state. Alloys with all-around effect are trained in this manner [13]. This is a type of two-way effect (Fig. 2d).

The pseudoelastic behavior is understood on the same basis. The $\beta \dashrightarrow \alpha$ transition is stress induced. Like the one-way effect, a selection of crystallographic shear potentials (Fig. 2, right, 3), occurs so that the shape change takes place in the direction of the best possible external shear tensor. The trend toward retransition $\alpha \dashrightarrow \beta$ is greater in this case than for the 1W effect. The operating temperature for pseudoelasticity must be somewhat higher above M_s than for the 1W effect.

The question arises of which alloys come into consideration as SM materials. The answer is: All those that exhibit a martensite transition (Table 1). This can be mixed crystals with polymorphous transition, like Ti, Mn, Fe and Co-alloys. Today the most frequently used materials are not based on these fundamental alloys. Rather, martensite transition intermetallic compounds of Cu or Ni with cubic, space-centered crystal structure of the high temperature phase β are used. It is notable for their technical application that in this case the martensite structure can be weaker than the austenite high temperature phase β. For stress effects ($\varepsilon \tilde{} 0$) the β-state is desired.

SMA based on titanium are known, but are rarely used. Here the transition also proceeds from a cubic space-centered mixed crystal. Materials based on Ti could become more important

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Table 3: Technical Applications of the Various Properties of SMA.

5 / 1	2 Einweg	3 Zweiweg	4 Pseudo-Elastizität
6 Verbindung / Befestigung	Rohrverbindungen, Spreizniete 14		24 Dichtungen, Brillenrahmen
7 Regelung		18 Ventilsteuerung, Wärme-Kälteschutz, Durchfluß, Gewächshaustemperatur	
8 Kraftfahrzeug		19 Öffnung von Nebellampen	25 hochdampfende Legierungen
9 Datenverarbeitung	15 Steckverbindungen für Schaltkreise	Kopf-Schreibsystem magn. Datenspeicher, Farbänderungen für opt. Speicherung	
10 Energie Motor		Wärmekraftmaschinen,	
11 Automation		21 Steuerung von Solarzellen	
12 Medizin	16 implantate Osteosynthese	22 Rotorglieder, Manipulatoren	26 Zahnspangen
13 Bekleidung	17 Verstärkung von Geweben	23 Endoskopsteuerung	

Key: 1-SME 2-one way 3-two way 4-pseudoelasticity 5-engineering 6-binding, attaching 7-control 8-motor vehicle 9-data processing 10-energy/engine 11-automation 12-medicine 13-clothing 14-pipe connections, spreader rivets 15-plug connections for circuits 16-implants (osteosynthesis) 17-tissue reinforcement 18-valve control, hot-cold protection, flow, greenhouse temperature 19-opening of fog lamps 20-head drive system of magnetic data storage, color changes for optical storage 21-heat engines, control of solar cells 22-rotor elements, manipulators 23-endoscope control 24-seals, glasses frames 25-high vapor pressure alloys 26-tongs

primarily because of secondary properties, like low weight, corrosion resistance and particularly bio-compatibility.

Of particular interest is the question of iron-based SMA (Table 1). These exhibit known crystallographic "reverse" transition behavior, like the established cubic space-centered alloys. They convert from cubic surface-centered lattice into space-centered or hexagonal structures. Excepting Fe, Pt and

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Table 4a-c. Symbols Used

a) Temperaturen der martensitischen Umwandlung. 22

M_s	1 Martensitbeginn beim Abkühlen	$\beta \rightarrow \alpha$
M_f	2 Martensitende beim Abkühlen	$\beta \rightarrow \alpha$
M_d	3 oberhalb M_d kein Martensit durch Verformung	$\beta_s \rightarrow \alpha_s$
A_s	4 Austenitbeginn beim Erwärmen	$\alpha \rightarrow \beta$
A_f	5 Austenitende beim Erwärmen	$\alpha \rightarrow \beta$
ΔT_H	6 Temperaturhysterese zwischen Hin- und Rückumwandlung	$\beta \rightarrow \beta$

b) Temperaturbereiche mit qualitativ verschiedenen mechanischen Eigenschaften der FGL. 23

T_1	$0\,K < T_1 < M_f < M_s$	7 2W-Effekt durch Erwärmen von T_1 aus, bis über A_f und Abkühlung unter M_f
T_2	$T_2 < A_s < A_f$	8 1W-Effekt durch Verformen bei T_2 und Erwärmen über A_f
T_3	$A_f < T_3 < M_d$	9 Pseudo-Elastizität durch Verformen bei T_3
T_4	$M_d < T_4 < T_5$	10 Normale Plastizität der β-Phase
T_5	$T_5 = T_4 > A_f$	11 Bereich diffusionskontrollierter Reaktion (Ausscheidung, Bainitbildung)
T_6	$T_6 > T_5$	12 Stabile homogene β-Phase (Betatisieren)

c) Kritische mechanische Spannungen und Formänderungen. 24

σ	13 irgendeine Zug- oder Druckspannung, entsche dend ist Schubspannungs-komponente in einem kristallographischen Scher system
R_s	14 wahre Streckgrenze der β-Phase (Austenit)
R_s	15 Streckgrenze der martensitischen α-Phase, sie kann höher oder niedriger sein als R_s
R_M	16 scheinbare Streckgrenze durch spannungsinduzierte Umwandlung $\beta \rightarrow \alpha$
$\Delta\sigma_H$	17 Spannungshysterese im pseudoelastischen Zustand
ε	18 irgendeine relative Formänderung
ε_{1W}	19 rel. Formänderung beim Einwegeffekt
ε_{2W}	20 rel. Formänderung beim Zweiwegeffekt
γ	21 Scherung bei der $\beta \rightarrow \alpha$-Umwandlung, $\gamma_{max} = \gamma = 2\,\varepsilon_{max}$

Key: 1-martensite begin upon cooling 2-martensite end upon cooling 3-above Md no martensite due to deformation 4-austenite begin upon heating 5-austenite end upon heating 6-temperature hysteresis between back and forth transition 7-two way effect due to heating from T1, to above Af and cooling below Mf 8-one way effect due to transition at T2 and heating above Af 9-pseudo-elasticity due to deformation at T3 10-normal plasticity of beta phase 11-region of diffusion controlled reaction (segregation, bainite formation) 12-stable homogeneous beta-phase 13-any tensile or compressive stress, shear component in a crystallographic shear system is decisive 14-true elastic limit of beta phase (austenite) 15-elastic limit of martensite alpha-phase, it can be higher or lower than 16-apparent elastic limit due to stress-induced transition 17-stress hysteresis in pseudoelastic state 18-any rel. shape change 19-rel. shape change for 1W effect 20-rel. shape change for 2W effect 21-shear for conversion 22-temperatures of martensite transition 23-temperature ranges with qualitatively different mech. properties of SMA 24-critical mechanical stresses and shape changes.

Fe-Pd alloys which probably cannot come into consideration as materials due to economic reasons, there are at present two developments for iron alloys. The first uses the transition into 492
a space-centered lattice. In order to obtain the needed reversibility of transition, a segregation treatment is needed in the high temperature phase [14, 15, 16]. This has been shown for FeNiAl, FeNiAlTi and FeNiCoTi alloys. The FeMnSi alloys developed by Nippon Steel are based on somewhat different principles. Here the cubic surface-centered lattice transforms into the hexagonal, densely packed phase (ε-martensite). This corresponds exactly to the conditions shown in Fig. 3 as an example for shear transition [17].

3. Preparation and Applications

Two aspects are important for technical application of alloys with shape memory:

1. They should be economically produced as semi-finished goods in constant, good quality.
2. Design principles and applications must be found appropriate to the special properties and limitations of the materials [4, 5, 6].

Table 2 shows some characteristics of alloys. It is clear that the NiTi-type is superior to the Cu alloys, if high strength is required. But the latter offer advantages when high electric conductance is desired (detachable connections in electronics).

An important aspect of quality, especially of alloys in which the 2W effect or pseudoelasticity is to be used, is the resistance to age and fatigue. Both in the conventional sense the formation of cracks must be expected, but also changes in transition behavior and thus temperature and hysteresis. Consequently, shape change properties can change during use of the alloys [18, 19].

The quality of materials depends very greatly on the chemical composition, the distribution of alloy elements and thus on the production conditions. Now it is very difficult to adjust the properties with an accuracy needed for many applications. This applies in particular for temperatures M_s and A_s. For example, the implantation SMA must tansform from alpha to beta exactly when body temperature is reached.

The alloys are usually prepared by melt metallurgy and plastic or milling processing as semifinished goods. Many efforts are aimed at powder-metallurgy production. Advantages are desired from uniform distribution of alloy elements and finer lattices. Through fast cooling of melts, thin bands or wires can be produced directly [20]. Perhaps it will be possible to use the SMA in the form of fibers or fabrics as components of composite materials [21], e.g. for manipulators.

One obstacle for the introduction of SMA on a larger scale is their high cost. This is due to metal prices, the difficulty of material production, and by the still small production quantities. Under these conditions, it is only feasible to produce a material and semifinished product if simultaneously a lucrative application

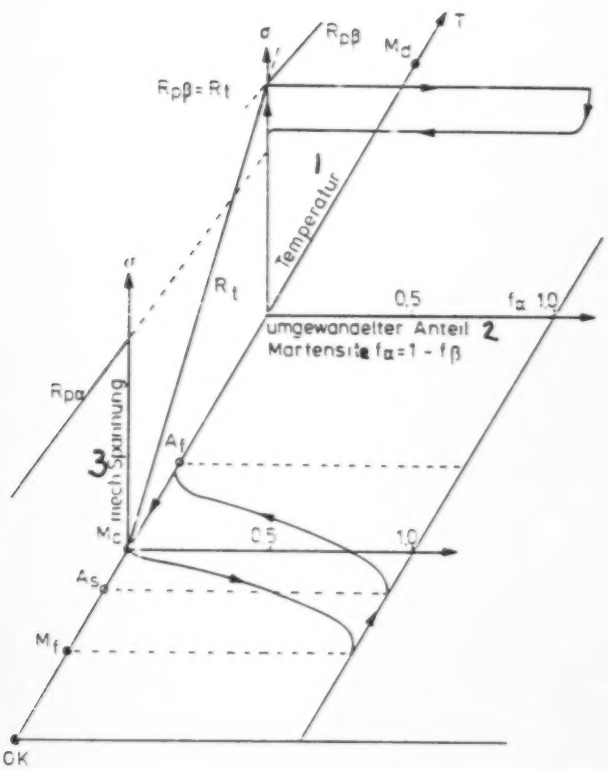

Fig. 5: Overview of the Different Shape Memory Properties as a Function of Stress and Temperature (Symbols in Table 4).

Key: 1-temperature 2-percent transformed 3-mech. stress

exists. To my knowledge there is only one manufacturer (Sept. 1986) which markets semi-finished goods (wires, tubes, bands, sheets) [22].

As became clear during the three conferences [4, 5, 6] the SMA offer solutions for which there are still no problems--i.e. no potential applications. But it is my impression that they will be found now in increasing numbers. If we wish to proceed systematically, it is useful to differentiate whether the 1W, 2W effect or pseudoelasticity is to be utilized, and also in what

area of engineering the application can be found. Some examples for this thinking are given in Table 3. But it does not contain all proven or possible applications. So a few of them will be discussed here.

The best known example for the use of the one-way effect is tube or other mechanical or electrical joints. A sleeve of SMA is cooled below M_f (α) and then expanded, so that it can be easily pushed over the joint parts. Upon reheating to $T > A_f$ (β), the part remembers its original shape and shrinks (perhaps vacuum-tight) onto the joint parts. NiTi alloys are best suitable for this because of their high strength. But recently, a CuNi alloy with Ti-Mn additives has been developed which comes close to the strength of NiTi [23]. Pins for plug connectors act similarly; they can be used quickly and reliably on microelectronic circuits.

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For heat or cold protection, spiral-coil components are used which expand or contract greatly at defined temperature (valve, lever). Fog headlights on motor vehicles open when switching on their lids, and windows of greenhouses open and close automatically due to the two-way effect at certain temperatures.

An unexplored area is SMA heat machines, although symposia have been held on the topic [24]. They are able to convert small temperature differences $\Delta T = M_f - A_f$ into rotation motion, however, only at low efficiency (~5%). Here too, the 2W effect is used. A spectacular application is in robot hands and other manipulators. Mechanical designs requiring many joints could be replaced by a wire with a memory for the desired motion. The role

of joints is assumed by the shear system in the crystals of the alloy (Fig. 2). Heating can be by direct passage of current.

The greatest number of applications of SMA is in medical engineering. They range from implants which remember the desired position of broken bones, bandages (1W effect), endoscope which can adapt its shape to intestinal windings (2W effect), up to tooth clasps which exert a uniform, defined pressure onto the corrected bite (pseudo-elasticity).

Finally, we mention that the technical introduction of these new materials wil require the cooperation of materials scientists, producers and users. In a number of countries (Belgium, China, France, Japan, USA) such cooperation is being federally supported (university-industry). Japan has come farthest in this development, and at present intensive efforts are under way on standardization of material types and on specifications for testing their properties [4].

Unfortunately none of that exists in our country. Increased efforts to remove this difficulty to make use of the new class of materials is surely desirable.

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